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Probing the Ordering of Semiconducting Fluorene-Thiophene Copolymer Surfaces on Rubbed Polyimide Substrates by Near-Edge X-ray Absorption Fine Structure

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The temperature-dependent alignment of semiconducting liquid crystalline (LC) fluorene-thiophene copolymer (F8T2) thin film surfaces on rubbed polyimide underlayers was investigated using the near-edge x-ray absorption fine structure (NEXAFS) technique. The NEXAFS data show that: a) in thin F8T2 films at all temperatures, the stiff polymer molecular axis lies in the plane of the substrate but the plane of conjugation of the F8T2 molecules is rotated randomly with respect to the surface normal, and b) after annealing in the LC phase the molecular axis is aligned with the rubbing direction of the rubbed polyimide alignment underlayer throughout the entire F8T2 film.

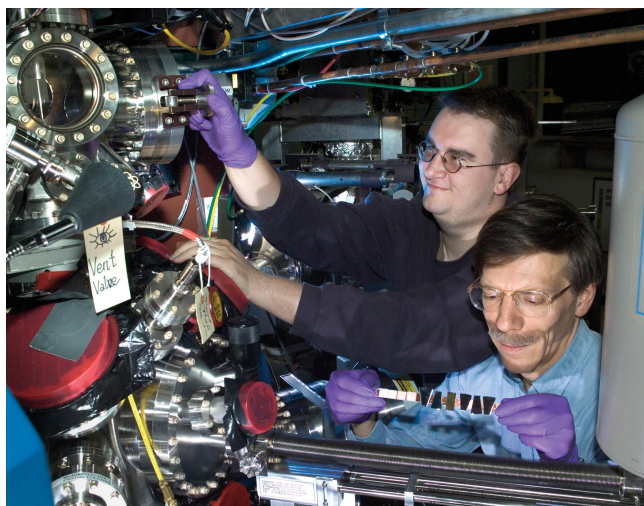
Conjugated organic polymers are increasingly being developed as functional materials for various devices including organic thin film transistors (OTFTs), photovoltaics, and organic light emitting diodes (OLEDs). Higher carrier mobilities and polarized photon emission are usually obtained when the conjugated polymer films are macroscopically ordered. Poly(9,9-dioctylfluorene-co-bithiophene) alternating copolymer (F8T2) has several characteristics that make it convenient for studying electrical characteristics of aligned polymer films: conjugated segments for charge transport, relatively good stability in air, and solubility in a wide range of solvents. It also exhibits a thermotropic liquid crystal LC phase.

Polarized UV-vis spectroscopy and polarized light microscopy showed that F8T2

thin films deposited on rubbed polyimide alignment layers can be macroscopically aligned when annealed in the nematic phase. The polymer chain alignment and charge carrier mobility for the F8T2 molecules presented in this study are strongly correlated. We found that when polymer chains were aligned parallel to the transistor channel length, the

field-effect mobility values are 2-3 times greater than mobility for as-deposited (amorphous) films, and 4-6 times greater than values obtained for devices with channel lengths perpendicular to polymer chain alignment.

Strong optical evidence of bulk polymer alignment on rubbed polyimide alignment layers exists, yet we do not know whether this alignment persists throughout the film to the surface. For certain device architectures in OTFTs, photovoltaics, and OLEDs, the alignment of the top surface will play a large role in the device performance. For instance, in OLEDs and photovoltaics, the F8T2 alignment affects charge injection and separation at the interfaces, and for non-inverted transistor structures, the top surface of the semiconductor is crucial



Authors (from left) Alex Hexemer and Daniel Fischer

to the carrier mobility, since this is the region of current flow in the transistor operation.

In this work, we look at the reorientation of fluorene-thiophene copolymer induced by deposition on a rubbed polyimide alignment layer after various thermal treatments. We use NEXAFS to determine the molecular orientation at the surface, observing the strong alignment of the F8T2 main-chain axis to the rubbing direction, and the temperature stability of these results.

The carbon K-edge NEXAFS spectra were recorded at angles $\theta=90^\circ$, 80° , 70° , 60° , 55° , 40° , 30° , and 20° , where θ is the angle between the electric field vector (E) of the polarized soft x-rays and the sample normal as well as the angle between the incident photon beam and the sample surface. Rubbing the polyimide aligns the surface molecules along the rubbing direction (RD), creating an asymmetry in the molecular bonds at the surface. The unidirectional

molecular alignment at the surface of the rubbed polyimide provides a template for the F8T2 orientation when heated to the mesophase. The NEXAFS spectra were recorded for two orientations of RD with respect to the plane of rotation E, parallel, where RD is always in the plane, and perpendicular, where RD is always normal to E.

In **Figure 1(a,b)**, we show the C K-edge NEXAFS partial electron yield (PEY) signal as a function of soft x-ray photon energy. The peak with strongest intensity at 284.4eV is the result of the transitions of electrons from the C1s to π^* orbitals of the conjugated C=C segments in the aromatic fluorene and thiophene rings. The transition dipole moment (TDM) of π^* orbitals is normal to the plane of conjugation. The NEXAFS PEY intensity at 20, 55, and 90° differed for the C=C 1s to π^* resonance at 284.4eV.

At 90° RD is parallel to the E of the incident soft x-ray radiation (parallel configuration). In this

case, absorption is low because the electric field vector lies along the main-chain axis, whereas the TDM of π^* orbitals are perpendicular to this axis. As expected, there is stronger absorption at a 20° angle of incidence, where a large component of E is out of plane, and the NEXAFS signal decreases with increasing angle. In the case of perpendicular geometry, the angular dependence provides information as to the orientation of the aromatic rings about molecular chain axis, i.e. are the rings in the plane of the substrate, normal to the surface or rotated at random? In this configuration, the sample is being rotated about the main-chain axis with respect to the electric field vector of the incident soft x-ray radiation. Absorption occurs when the TDMs of the π^* orbitals are parallel to the E of the incident light. In Figure 2b, we see that the 20° , 55° , and 90° C1s to π^* resonances overlap. This indicates that the orientation of the aromatic rings at the surface is nearly random.

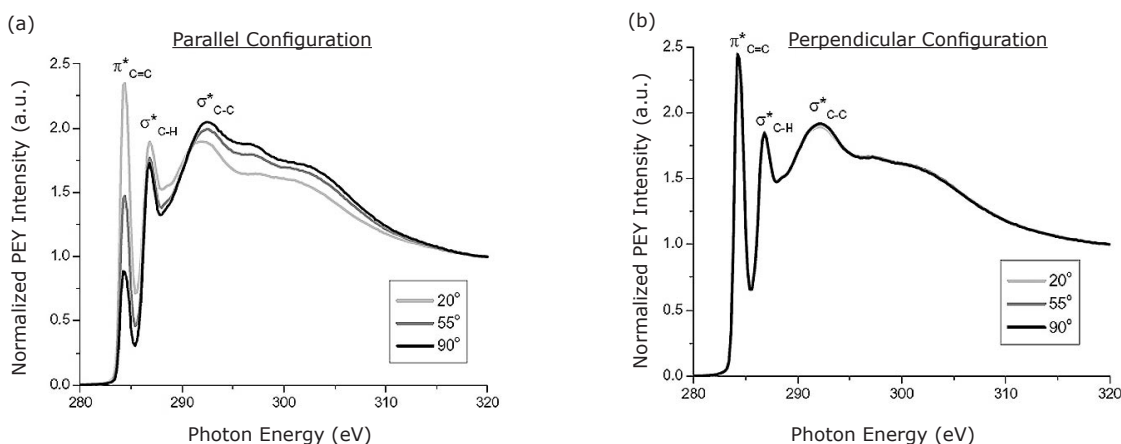


Figure 1. Partial electron yield data for F8T2 thin film sample that was annealed at a temperature of 280°C , then quenched to room temperature. Scans taken at room temperature at $\theta = 20^\circ$, 55° , and 90° incidence in the parallel (a) and perpendicular (b) geometries. The strong overlap of curves in (b) makes it difficult to distinguish between the three scans.